

STUDY OF REACTION MECHANISMS IN CELLULOSE PYROLYSIS

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Introduction

As the concerns for energy supply and the pollution problems caused by burning fossil fuels become more pronounce, a great deal of attention has been paid to using renewable and clean fuels at present, including the use of biomass. Among alternatives of using biomass as an energy source, the thermo-chemical conversion appears to be a promising route, which includes pyrolysis, combustion, and gasification. Pyrolysis is not only the initial process of gasification and combustion, but also an individual technique to form high energy density products in which biomass goes through physical and chemical changes to produce gas, char and bio-oil when it is heated in an inert atmosphere. Researching the reaction mechanisms of biomass pyrolysis would provide a better understanding of the process and be beneficial for the optimization of reaction parameters and reactor design. This study aims at modeling the cellulose pyrolysis and developing simulations to optimize the reaction conditions.

All biomass contain a great ratio of cellulose, and being the major component in biomass, cellulose behaves the whole decomposition regulation of biomass in pyrolysis. So many mechanism researches on biomass pyrolysis are taken with cellulose.

Experiment instruments

In order to study the chemical reaction and mechanism in cellulose pyrolysis, a series of experiments are made on the cellulose material rolled as cylinder in a quartz glass reactor concentric with a silicon carbide pipe (shown in the figure 1), which supplies the heat required in cellulose pyrolysis by radiation through the transparent quartz glass at a maximum electric power of 8KW. In the reactor system, the char is trapped in a char-collection, while the volatile flows with carrier gas into three-stage condensers, which are dipped in a mixture of dry ice with acetone. The condensable volatile condensed into bio-oil when flowing through the condensers, while the incondensable volatile is discharged out and collected into a gasbag for GC analysis. The yields of char, bio-oil and gas in different reacting condition are obtained by controlling the radiant source temperature (RST) and carrier gas flow, and the important components yields in bio-oil also are measured by a quantitative analysis through GC-MS.

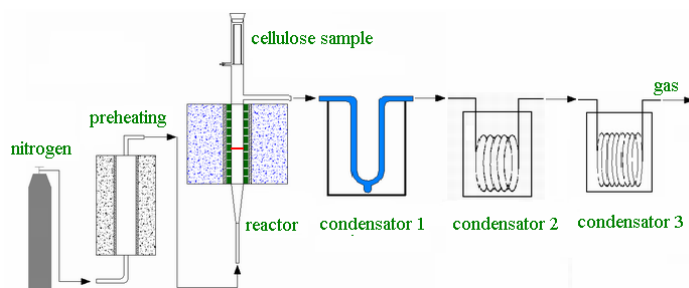


Figure 1. Cellulose fast pyrolysis system

Model Conception

Analyzing the data, a modified kinetic mechanism is brought out basing on the Brodio-Shafizadeh (B-S) mechanism [1], which is described as followed (shown in figure 2): In the initial stage of cellulose pyrolysis, Active cellulose (AC) was formed accompanied by reduction of polymerisation degree of cellulose. If reaction temperature is low, AC will change into charcoal by dehydration.

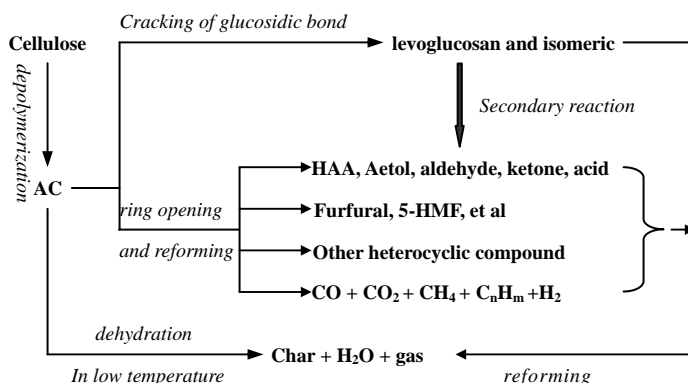


Figure 2. The modified B-S mechanism

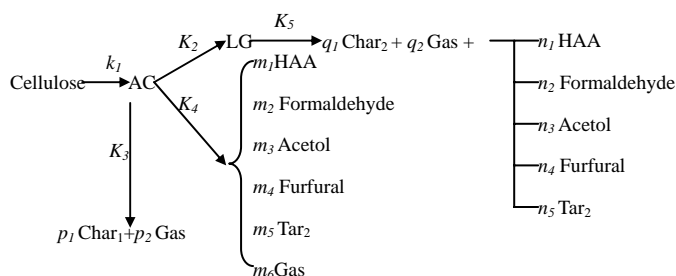
As temperature rises higher, AC decomposed by two competitive reactions, cracking of glucosidic bond or opening and reforming of pyranoid ring. Cracking of glucosidic bond will produce levoglucosan (LG) and its isomeric anhydrosugar. At same time, opening of acetal structural ring and cracking of internal C-C bond in pyranoid ring will bring into the formation of hydroxyl-acetaldehyde (HAA), acetol, furfural, CO and other small compounds. Compared with the formation of anhydrosugar, opening and cracking of ring was higher in active energy. At the situation of long gaseous residence, anhydrosugar will undergo secondary decomposition similar with the opening and reforming of pyranoid ring in AC and produce small molecule gas, secondary char and secondary bio-oil which includes almost all the competitive products of AC by reforming of pyranoid ring.

According to the experimental system's feature, when cellulose decomposes, volatile and gas will escape from the solid fabric, then flow into the gas space in reactor and occur the secondary reaction, so the model includes two major parts: the primary react stage in the cellulose fabric structure and the secondary react in gas space. Since other pyrolysis systems also have the solid and gas space, the

conception of this model is also applicable to them. The kinetic model used in gas space for volatiles is the same with the model in solid space. Basing on the modified B-S mechanism, a detail model is made with two stages to simulate the evolving process and path of cellulose, AC, char, gas, LG, HAA, acetol, formaldehyde and furfural which are all the most important compounds in pyrolysis process, and the other volatiles are put together as tar2 (as shown in figure 3).

Figure 3. Kinetic model basing on modified B-S mechanism

In these competitive reacts, the reaction coefficient of each



components in K_4 is difficult to be determined, however, they could be obtained by extrapolation of the yield to infinite radiant source temperature. In ideal case, if cellulose was heated at a very high rate to an infinite temperature, and volatile released from cellulose had a very short residence, secondary cracking could be ignored reaction, and the competitive reactions K_4 will take the predominant role in AC consuming process since they have high active energy than the K_2 reaction. Thus, reaction coefficient could be obtained by calculating product's yield at this ideal case, and their ratio is acceptable to the secondary reaction of LG, while the other reaction coefficients such as p_1 , p_2 [2] and react kinetic constants (E_i , A_i) [1,3,4,5], reaction heat (ΔH_i) are selected from literatures [6]. The ratio q_1 , q_2 are calculated from the experiments of LG pyrolysis results which don't show in this paper.

Making the feature of this reactor system as the boundary condition of this model, the continuity differential equations and energy conservation differential equations in solid space and gas space are listed respectively. Only cellulose, AC, LG and HAA continuity differential equations in solid space are presented below, other compounds or in gas space are similar with them, so these equations are neglected in the paper.

$$\frac{\partial \rho_{\text{Cellulose}}}{\partial t} = -k_1 \cdot \rho_{\text{Cellulose}} \quad (1)$$

$$\frac{\partial \rho_{\text{AC}}}{\partial t} = k_1 \cdot \rho_{\text{Cellulose}} - (k_2 + k_3 + k_4) \cdot \rho_{\text{AC}} \quad (2)$$

$$\frac{\partial \rho_{\text{LG}}}{\partial t} + \frac{2}{\delta} \cdot (\rho_{\text{LG}} \cdot u_f) = k_2 \cdot \rho_{\text{AC}} - k_5 \cdot \rho_{\text{LG}} \quad (3)$$

$$\frac{\partial \rho_{\text{HAA}}}{\partial t} + \frac{2}{\delta} \cdot (\rho_{\text{HAA}} \cdot u_f) = m_1 \cdot k_4 \cdot \rho_{\text{AC}} + n_1 \cdot k_5 \cdot \rho_{\text{LG}} \quad (4)$$

All reaction rate constants K_i would be described by Arrhenius Equation, which is expressed by $K_i = A_i \exp(-E_i/RT)$, While u_f in above equations represented gas apparent flow in the void of material,

which could be calculated by Darcy Law, R is the gas constant number.

The heat required during cellulose pyrolysis was mainly supplied by thermo-radiation from silicon carbide pipe and by heat convection between carrier gas and material surfaces. In addition, reaction heat in primary reaction and secondary cracking also had influence. As was shown in Equation 5.

$$\frac{\partial}{\partial t} (T \sum \rho_i C_i) + \frac{1}{\delta} (T \sum \rho_i C_i u_i) = \frac{2}{\delta} \cdot (\alpha_f (T_f - T) + \varepsilon_0 \cdot \sigma (T_{\text{TRS}}^4 - T^4)) + Q_{\text{react}} \quad (5)$$

Where T represented temperature of solid material, while T_f and T_{TRS} the temperature of carrier gas and radiator. C corresponded to specific heat capacity. α_f is the heat convection coefficients between carrier gas with material surfaces. σ is the Stefan-Bolzman constant, and ε_0 referred to black degree of cellulose material. Q_{react} could be described by following Equation 6.

$$Q_{\text{react}} = k_0 \Delta H_0 \rho_{\text{Cellulose}} + (k_1 \Delta H_1 + k_2 \Delta H_2 + k_3 \Delta H_3) \rho_{\text{AC}} + k_4 \Delta H_4 \rho_{\text{LG}} \quad (6)$$

According this methods and conception, the paper simulates the pyrolysis behavior of the cylindraceous cellulose about 0.18 mm thickness, including the formation, development or evolution of major compounds in the condition of 700~1300K radiant source temperature, 100~700L/h carrier gas flow

Modeling Results

The simulating results show that the temperature of cellulose material in the reaction process divides into three stages. At the initial stage, all reactions have a low rate and cellulose is heated rapidly by radiation in a pure physical heating method until the temperature reaches about 690K, then the primary decomposing reaction increases its rate, which absorbs almost all the heat transferred by radiation and restrains the increasing of reaction temperature. Even in the high radiant source temperature about 880K, this endothermic effect is still strong and makes cellulose locating in the low temperature about 690~720K during the whole primary reaction stage. At the last stage, the primary pyrolysis is finished and the temperature returns to a high promotion until reach to the equilibrium with surroundings. From the result, we can suppose that in the pyrolysis or gasification techniques, the material's temperature is a variational parameter for the reaction heat effect, so a thermocouple with general response sensitive will induce a measure error.

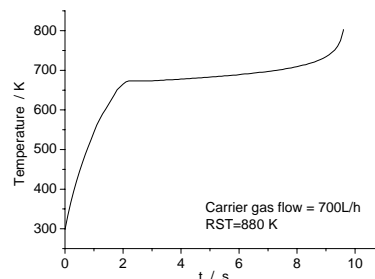


Figure 4. Temperature Vs time

The consumption rate of cellulose is responding with the reacting temperature, and converted completely at the prophase of the second stage. According to the modified B-S mechanism, the transforming of cellulose is only the initial stage; the leading actor deciding the process evolvement and products distribution is this middle component, active cellulose, whose density and temperature determine the evolving rate of the competitive reaction paths by cracking of glucosidic bond or reforming of pyranoid ring.

Figure 5 shows the rules of cellulose and AC converting process, a maximum AC density is just arrived when cellulose is consumed out in middle stage of the process. Comparing figure 5 with figure 4, the beginning point with the third stage of temperature is just when AC consumed away, the coincidence shows it is the endothermic decomposition of AC decides the development of pyrolysis process.

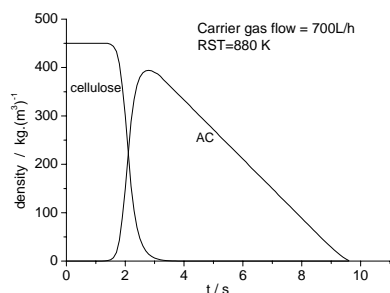


Figure 5. Products' density vs temperature

Char is formed by two ways, one is the dehydration of active cellulose in the low temperature into dehydrated cellulose, which then reformed into primary char and emit gas, the primary char is dependent upon the temperature history of AC and keep the fabric structure of cellulose; the other is coming from the secondary cracking and reforming of LG or other primary volatile. Cellulose, AC, and the primary char form the holing structure in the solid space, in which LG and the other primary volatile occur the secondary reaction when flowing through the holing structure and partially convert into secondary char. So the evolving process of secondary char in solid space is proportional to the density of primary volatile and solid temperature. From calculating, in the condition of radiant resource temperature below 1100K, the temperature of cellulose material is focused between 700~820K, and the secondary react in holing structure is ignorable in the given cellulose thickness (As shown in figure 6).

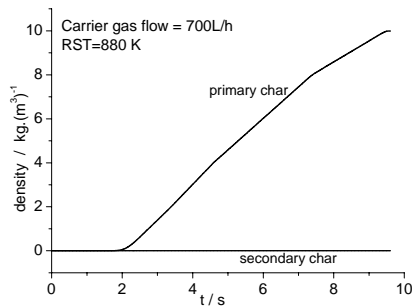


Figure 6. Products' density vs temperature

Being the product of AC by cracking of glucosidic bond in the middle temperature, LG is not only the desiring product in pyrolysis technique but also a precursor of the other volatile, whose formation and evolvement have the same status as AC in the pyrolysis process. The evolvement of LG is dependent upon the integrate effect of reaction rate, conversion degree of AC, local temperature and flow rate of volatile. In the initial stage of pyrolysis, the formation of LG is small and slow for the restrain of low temperature. With the temperature rising, its forming rate and flowing rate from interior to outside increase, which induces a rapid formation and fast flow of LG. Upon the effect of these two process synthetically, LG maintains a stable density for a relatively long time in the middle stage of pyrolysis process. Then AC is going to be consumed out, and a rapid decrease of LG density occurs caused mainly by the fast outward flowing rate.

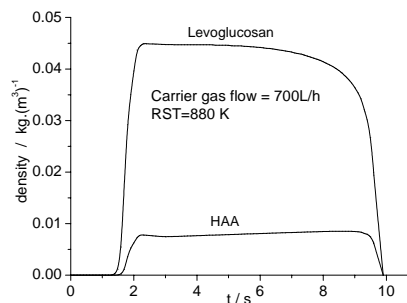


Figure 7. Products' density vs temperature

Similar with LG, the competitive products such as HAA, acetol, formaldehyde and furfural also show a rapid growing and fast flowing process in the middle stage. But they have a slow stepping up in the relatively stable stage, comparing with the stepping down tendency of LG, which just shows the superiority of competitive reaction by the opening and reformation of pyranoid ring in higher temperature. Figure 7 only shows the density distribution of HAA, other compounds are neglected for the same tendency. Since the reaction temperature is restrained in a middle range by endothermic reaction, LG dose not occur abundant secondary cracking in the solid space, so almost all the competitive products are coming from the splitting and reforming of pyranoid ring in AC.

LG and other volatiles escaped from solid space will flow into the gas space taken by carrier gas, and occur the secondary pyrolysis. The gas space is large and some assumption must be made to simple the model, so six controlled volumes are set to simulate the secondary reacting process.

From the results, a similar tendency of gas temperature and volatile density are obtained that they are all transferred from the reactor bottom to the outlet one controlled volume by one controlled volume. And in the carrier gas flow about 700L/h, a very short gas resident time about 0.12 second induces little secondary reaction of LG and almost no difference of volatile density in the six controlled volumes is founded (shown in figure 8), which is just the reason why the pyrolysis technique must keep a very short gas resident time to maximum the yield of bio-oil.

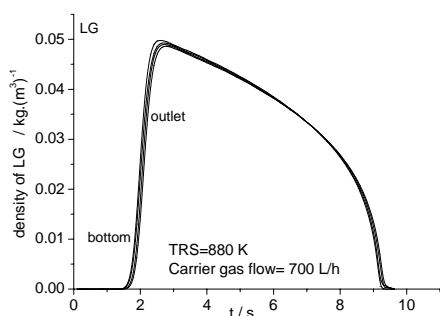


Figure 8. LG density vs time in gas space (short resident time)

Simulation on the condition of middle temperature and large carrier gas flow shows us that neither in the fabric solid space, nor in the gas space, the secondary reaction takes place. So in this conditions, the yield increasing of HAA and acetol with temperature rising is not coming from the secondary cracking of LG, but from the competitive consuming of AC by splitting and reforming of pyranoid ring. This simulating result improves the parallel competitive mechanism in the volatile forming process from another view.

With a small carrier gas flow about 100L/h, a very slow flowing rate make a decreasing of LG density and improving of other volatiles density, this tendency transfers upward one by one and pricks up with temperature rising (shown in figure 9).

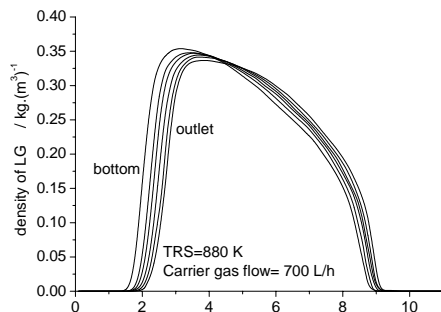


Figure 9. LG density vs time in gas space (long resident time)

Contrary with the decreasing of LG, the distribution of HAA, acetol, formaldehyde in gas space is increasing by degrees with the react time (shown in figure 10), which proves the consumption of LG is supplied to the competitive products by cracking of pyranoid ring. But their increasing tendency is not so intensive as the decreasing of LG since they also occur secondary reaction in the high temperature to form smaller components and gases.

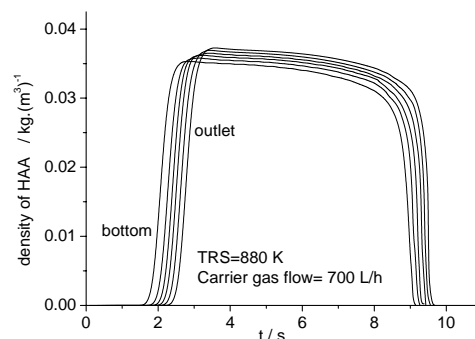


Figure 10. HAA density vs time in gas space (short resident time)

Integrating the density from reactor outlet and flow rate with time will get the yield of compounds. Synthesizing effect of RST and carrier gas flow on pyrolysis process, a good agreement with the experimental results is obtained. Viewing as a whole, in the technique to produce bio-oil, particularly to obtain a high yield of LG, a middle temperature about 700~950K and gas resident time less than 1.0 second is the necessary condition. Temperature has a stronger effect than gas resident time on HAA, acetol, formaldehyde and furfural, and higher temperature is benefit to their formation.

Conclusions

A series of experiments have been done in a thermal radiant reactor system to study the mechanism of cellulose pyrolysis process, and the forming rules of some important compounds with reaction condition were obtained. Analysis these data, a modified reaction mechanism was brought out from the B-S mechanism model. Combining with the common feature of pyrolysis or gasification equipments with two reaction spaces, a synthesis model with two stages was build to simulate the decomposing and evolving process of AC, LG, HAA, Acetol and furfural in bio-oil.

All reaction and evolvement of compounds are dependent upon the reaction temperature, and the simulating results show that cellulose material is restrained in middle temperature during the major reaction zone for a strong endothermic of primary decomposition. This function is still in effect even in the high RST about 1100K, and so benefits the formation of bio-oil, while decreases the probability of primary volatile cracking into small gas by secondary reactions. So the difference of products density in solid space is evidently due to the competitive ability of different primary reactions, and the secondary reactions have little effect on the products distributions. Increasing the thickness of cellulose, delaying the resident time of primary volatile in fabric structure or enhancing the intensity of heat transfer will improve the temperature of cellulose, and benefit the cracking and opening-ring reactions of pyranoid ring in AC, which decrease the yield of LG.

Almost all the secondary reaction occurs in gas space in this experimental condition, in RTS about 880K and carrier gas flow about 700L/h, the LG escaping from fabric holes seldom happens secondary cracking, but fall the carrier gas flow down to 100L/h, 4.78% LG decomposes in to small compounds and this effect

improves with RST. So an optimum condition for LG yield is obtained about 730K~920K, in addition, the less resident time of volatile staying in reactor, the more yield can be collected since LG is very easy to split into small compounds. Temperature has a stronger effect than gas resident time on HAA, acetol, formaldehyde and furfural, and higher temperature is benefit to their formation.

All these results provide a foundation for the optimization of reaction parameters and reactor design.

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